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SURFACE ANALYSIS OF β-HMX

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INTRODUCTION

HMX is an important ingredient in many military and commercial propellants and explosives. Various size classes are available from the vendor and microscopical observations of Class A HMX (a large size) in cross polarized light showed that many of the large HMX crystals had a nonuniform, dark amorphous coating as well as small particles adhering to the surface of the larger size HMX. The small particles most likely were HMX fines. The nature of the amorphous coating was unknown. Subsequent crushing of large HMX particles made any detection of the coating impossible on the fractured particles. Those particles which escaped fracture retained both fine particles and coating.

The coating and fine particles found on the surface of large HMX crystals have now been identified. Infrared analysis showed that the fine crystals adhering to the surface of large HMX was RDX enriched HMX. Transmission electron microscope analysis placed the particle size of these fines in the .05 to .2 micron range. The amorphous coating was identified as a long chain aliphatic ester-oil. Examination of the shipping bags used for HMX showed a long chain aliphatic ester and was identified as beeswax. The beeswax is soluble in isopropyl alcohol and somewhat in water which explains how beeswax is transmitted to the HMX particles. HMX is shipped either water or isopropyl alcohol wet. A second sizing found on the bags but not on the HMX crystal was a methyl silicone. This silicone is insoluble in water and isopropyl alcohol and was not detected on the HMX. The estimated concentrations of RDX fines was 0.1% and the beeswax 0.01%.

FUTURE WORK

No further work is planned.

DISCUSSION

Optical Microscopy

Large crystals of β HMX examined under cross polarized light had two surface unknowns as shown in Figure 1.

Figure 1. Coating on Large HMX

One of the unknowns was a non uniform amorphous coating. The second unknown consisted of sub-micron crystals adhering to the host particle. These microcrystals were thought to be very fine particle HMX. Attempts to identify these unknowns were unsuccessful in the past due to the inability to recover the unknowns in sufficient quantity free of HMX. This investigation was successful in recovering and identifying these unknowns from the surface of large particle HMX.

The initial approach was with optical microscopy followed by transmission electron microscopical and infrared analysis.

Electron Microscopy

Transmission electron microscopy was selected over scanning techniques because past experience has shown that microcrystalline material is easily lost or altered in the electron beam or during preparation of the sample. In transmission microscopy a replica of the surface can be made and thus none of the bulk samples is ever in direct contact with the electron beam. The technique used to prepare these samples for transmission electron microscopy is now described.

Representative crystals of HMX classified by sieves into +200 and +150 micron fractions, were placed on a clean glass microscope slide. Acetone was added dropwise to one side of a small (1") piece of clean cellulose acetate film to partially dissolve the surface. After several seconds, while still partially soft, the strip of moistened cellulose acetate was placed over the sample on the microscope slide and gently pressed into the crystals. After 5 minutes, when completely dry, the cellulose acetate was stripped from the slide carrying with it the crystals partially embedded in the surface. These crystals were gently teased away from the tape with a wooden dowel, leaving behind an exact imprint of their surfaces in the cellulose acetate plus loosely adherent particles or coatings. These replicas were taped flat to a glass slide, placed in a vacuum evaporator and shadowed with a thin chromium film (2-30 nm thick, operating vacuum about 10^{-6} Torr). The shadowed replicas were then coated at normal incidence with a vacuum deposited layer of carbon. The cellulose acetate support film was then dissolved, leaving a carbon/metal replica of the crystal surfaces suitable for penetration by the electron beam.

Subsequent examination by transmission electron microscopy at 30,000 times magnification showed rough, pitted surfaces on the HMX, plus frequent microcrystals (averaging between 0.05 and 0.2 micron in size) adhering to the surface and dark, amorphous-appearing patches resembling a thin, oily film (Figure 2).

Figure 2. Transmission Electron Photomicrograph, 30,000 X

Solvent Extraction and Infrared Analysis of HMX and Cloth Bags Used for HMX Storage (Shipping)

High purity solvents (diethyl ether and absolute alcohol) were used as solvents to extract several lots of HMX. These solvents were selected because of their low residue content and the relative insolubility of HMX in these solvents. The HMX is shipped wet either in isopropyl alcohol or water packed in rubber bags with cloth inserts. Thus it was natural to suspect that at least one of these contaminants came from either the cloth or rubber shipping bags.

Extraction of certain lots of HMX with ether or alcohol showed the expected RDX impurity and a small amount of aliphatic hydrocarbon and carbonyl. Since the hydrocarbon species was believed to originate in the cloth bags used to store and ship HMX, subsequent extractions were made of the HMX shipping bags which contained a fair amount of surface HMX. The IR spectrum in Figure 3 shows this dried ether extract of an HMX storage bag.

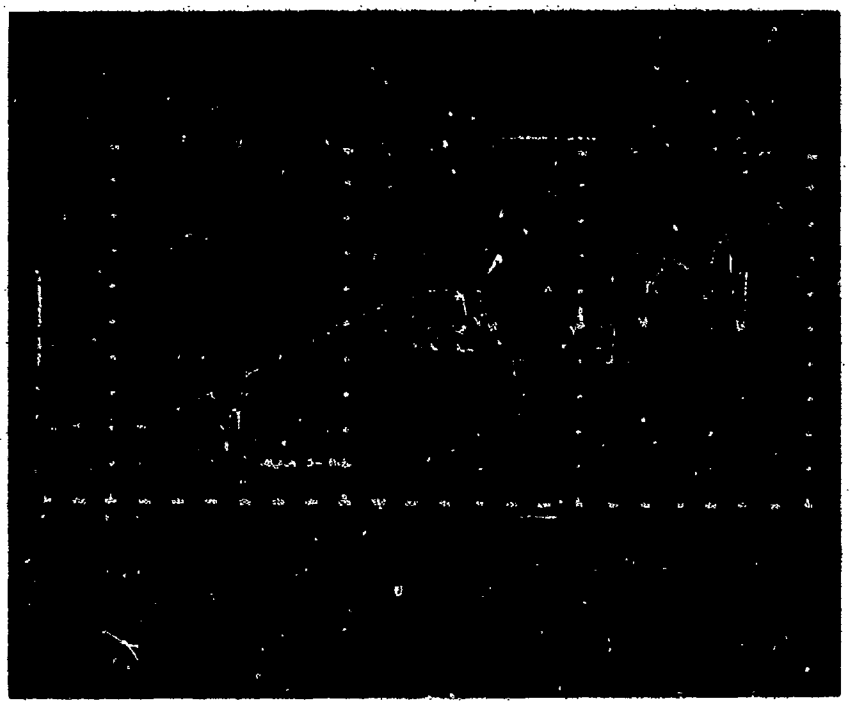

Figure 3. IR Scan of Dried Ether Extract of HMX Storage Bag.

Some fine HMX was carried over and is obvious in the spectrum. Also noted in the spectrum was a large amount of aliphatic C-H stretching absorbance at 2950 cm^{-1} and a small amount of carbonyl absorbance near 1740 cm^{-1}. These peaks were not found to any extent in the spectrum of a solvent residue and do not exist in HMX.

Upon receipt of a sample of the cloth bag from the vendor, an ether extraction yielded a spectrum shown in Figure 4. The same cloth extracted with alcohol yielded the spectrum shown in Figure 5.

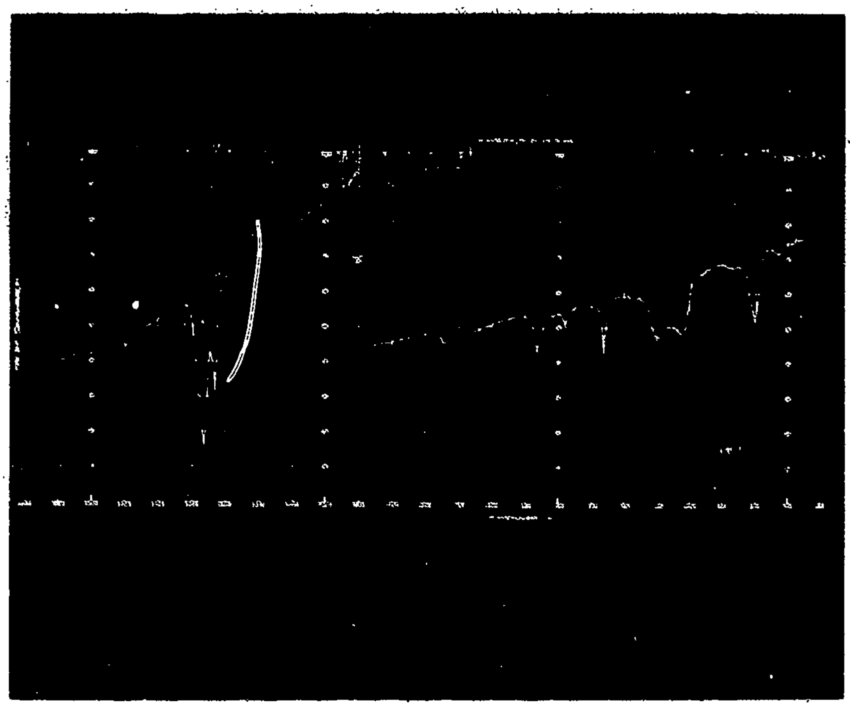

Figure 4. IR Scan of Dried Ether Extract of New Cloth Bag

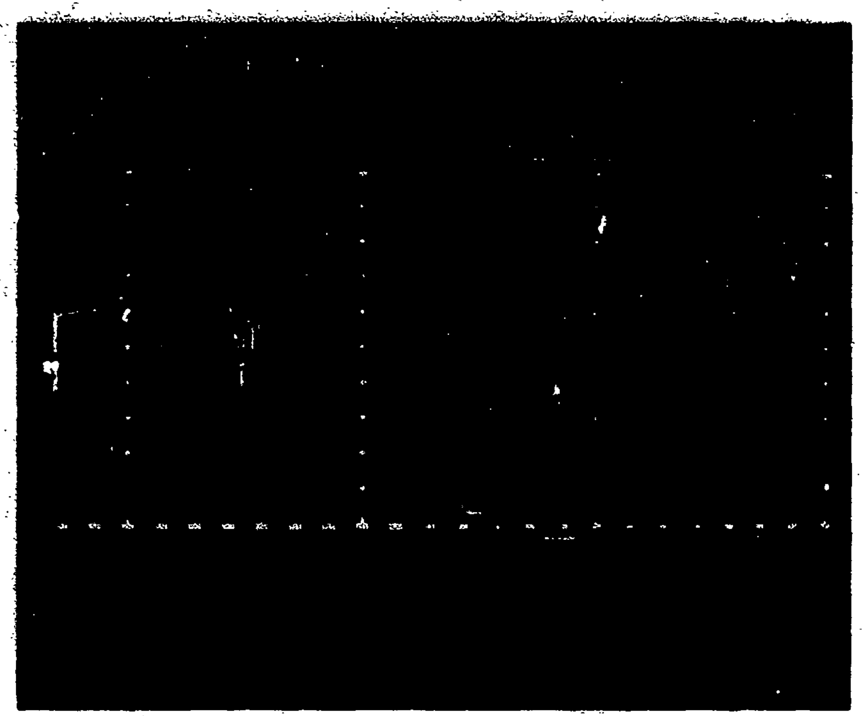

Figure 5. IR Scan of Ethanol Extract of New Cloth Bag

The analysis of these spectra shows that the sizing on the cloth consisted of both a long chain aliphatic ester oil plus an aliphatic silicone oil. The total sizing content averaged in the 0.5 percent range.

The identification of the ester-oil component of the sizing was assigned to a beeswax type compound. This is a complex mixture of long chain aliphatic esters. A spectrum of beeswax is shown in Figure 6 for comparison.

Figure 6. IR Spectrum of Beeswax

This shows the aliphatic C-H stretching and carbonyl bands which were noted in the HMX alcohol extract. Since this work was completed the vendor did report the use of beeswax and silicone oil on the shipping bags. Fortunately the silicone oil is not soluble in the solvents used for shipping the HMX. The presence of a silicone could have significant effects on the binding properties of HMX to an explosive mixture. Only estimates of the quantities of RDX and beeswax could be made because they cannot be recovered free of HMX. The estimated percentage of RDX fines is 0.1% and beeswax 0.01%.

CONCLUSIONS AND RECOMMENDATIONS

The surface contaminates of HMX as received from the vendor have been identified as beeswax and submicron HMX enriched with RDX. Their presence should be taken into consideration for the end use of the HMX.